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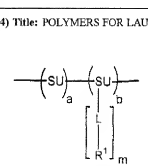
(54) Title: POLYMERS FOR LAUNDRY APPLICATIONS



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(57) Abstract: The present invention relates to use of a compound for promoting soil release during laundering of a textile fabric, the compound being a polymer having the general formula (I) characterised in that each SU represents a sugar unit in a polysaccharide backbone; a represents the number of unsubstituted sugar units as a percentage of the total number of sugar units and is in the range from 0 to 99.9%, preferably 65 to 99%, more preferably 80 to 99%; b represents the number of substituted sugar units as a percentage of the total number of sugar units and is in the range from 0.1 to 100%, preferably 1 to 35%, more preferably 1 to 20%; m represents the degree of substitution per sugar unit and is from 1 to 3; L represents an ester or ether linkage; and R1 represents a substituted alkyl group, preferably a hydroxyalkyl, carboxyalkyl or sulfoalkyl group or a salt thereof. A method of promoting soil release during laundering of a textile fabric and the use of such polymers in the manufacture of a laundry cleaning composition for effecting soil release from a laundry item form other aspects of the invention.

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POLYMERS FOR LAUNDRY APPLICATIONS

Technical Field

The present invention relates to substituted polysaccharides which are used in laundry cleaning products, for instance, for incorporation in products for dosing in the wash and/or rinse. These polymers are intended for, but not limited to, soil release benefits in such products.

Background of the Invention

The term "soil release polymer" is used in the art to cover polymeric materials which assist release of soil from fabrics, e.g. cotton or polyester based fabrics. For example, it is used in relation to polymers which assist release of soil direct from fibres. It is also used to refer to polymers which modify the fibres so that dirt adheres to the polymer-modified fibres rather than to the fibre material itself. Then, when the fabric is washed the next time, the dirt is more easily removed than if it was adhering the fibres. Although not wishing to be bound by any particular theory or explanation, the inventors believe that the soil release polymers utilised in the present invention probably exert their effect mainly by the latter mechanism.

The compounds utilised by the present invention have been found, dependent upon the structure of the compound in question, to deliver a soil release, fabric care and/or other laundry cleaning benefit.

The deposition of a benefit agent onto a substrate, such as a fabric, is well known in the art. In laundry applications typical "benefit agents" include fabric softeners and conditioners, soil release polymers, sunscreens; and the like. Deposition of a benefit agent is used, for example, in fabric treatment processes such as fabric softening to impart desirable properties to the fabric substrate.

Conventionally, the deposition of the benefit agent has had to rely upon the attractive forces between the oppositely charged substrate and the benefit agent. Typically this requires the addition of benefit agents during the rinsing step of a treatment process so as to avoid adverse effects from other charged chemical species present in the treatment compositions. For example, cationic fabric conditioners are incompatible with anionic surfactants in laundry washing compositions.

Such adverse charge considerations can place severe limitations upon the inclusion of benefit agents in compositions where an active component thereof is of an opposite charge to that of the benefit agent. For example, cotton is negatively charged and thus requires a positively charged benefit agent in order for the benefit agent to be substantive to the cotton, i.e. to have an affinity for the cotton so as to absorb onto it. Often the substantivity of

the benefit agent is reduced and/or the deposition rate of the material is reduced because of the presence of incompatible charged species in the compositions. However, in recent times, it has been proposed to deliver a benefit agent in a form whereby it is substituted onto another chemical moiety which increases its affinity for the substrate in question.

The compounds used by the present invention for soil-release and/or other benefits are substituted polysaccharide structures, especially substituted cellulosic structures.

Recently, substituted cellulosic oligomers and polymers have been proposed as ingredients in laundry products for providing a variety of different benefits such as fabric rebuild, as disclosed in WO-A-98/29528, WO-A-99/14245, WO-A-00/18861, WO-A-00/18862, WO-A-00/40684 and WO-A-00/40685.

US-A-4 235 735 discloses cellulose acetates with a defined degree of substitution as anti-redeposition agents in laundry products.

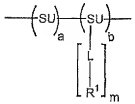
Cellulosic esters are also known for use in non-laundry applications, as described in WO-A-91/16359 and GB-A-1 041 020.

It has previously been recognised in the art that cellulose based materials adhere to cotton fibres. For example, WO 00/18861 and WO 00/18862 disclose cellulosic compounds having a benefit agent attached, so that the benefit agent will be attached to the fibre. See also WO 99/14925.

However, the ability of polysaccharide, especially cellulose, based materials to adhere has not been fully investigated, and a need exists to find polysaccharide based materials that are of commercial significance.

Definition of the Invention

A first aspect of the present invention provides use of a compound for promoting soil release during laundering of a textile fabric, the compound being a polymer having the general formula



(I)

in which each SU represents a sugar unit in a polysaccharide backbone;

a represents the number of unsubstituted sugar units as a percentage of the total number of sugar units and is in the range from 0 to 99.9%, preferably 65 to 99%, more preferably 80 to 99%;

b represents the number of substituted sugar units as a percentage of the total number of sugar units and is in the

range from 0.1 to 100%, preferably 1 to 35%, more preferably 1 to 20%;

m represents the degree of substitution per sugar unit and is from 1 to 3;

L represents an ester or ether linkage; and

R^1 represents a substituted alkyl group, preferably a hydroxyalkyl, carboxyalkyl or sulfoalkyl group or a salt thereof.

This aspect of the present invention may also be expressed as a method of promoting soil release during laundering of a textile fabric, the method comprising contacting the fabric with a polymer as defined above, preferably in the form of a laundry cleaning composition comprising said polymer, and most preferably in the form of an aqueous dispersion or solution of said composition, and subsequently washing the fabric after wear or use of the fabric.

In addition, this aspect may be expressed as use of a compound in the manufacture of a laundry cleaning composition for effecting soil release from a laundry item, the compound being a polymer as defined above.

A second aspect of the invention provides a polymer as defined above for deposition onto a fabric during a laundry cleaning process.

The second aspect of the invention may also be expressed as a method of depositing a benefit agent onto a fabric, the

method comprising applying a polymer or a composition as defined above to the fabric.

In the context of this specification, the terms "cleaning" or "laundering" mean "washing and/or rinsing".

It will be appreciated that the group $-L-R^1$ is a relatively small substituent of relatively low molecular weight compared to many of the groups which have been used as substituents for polysaccharides in the prior art.

Detailed Description of the Invention

Definitions

The following definitions pertain to chemical structures, molecular segments and substituents:

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group which may contain from 1 to 12 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl etc. More preferably, an alkyl group contains from 1 to 6, preferably 1 to 4 carbon atoms. "Substituted alkyl" refers to alkyl substituted with one or more substituent groups. Preferably, alkyl and substituted alkyl groups are unbranched. An "alkenyl" group is a branched or unbranched unsaturated hydrocarbon containing 1 to 12, preferably 1 to

6 and especially 1 to 4 carbon atoms. Preferably, alkenyl and substituted alkenyl groups are unbranched.

A halogen atom may be a fluorine, chlorine, bromine or iodine atom and any group which contains a halo moiety, such as a haloalkyl group, may thus contain any one or more of these halogen atoms.

As those of skill in the art of polysaccharide, especially cellulosic, polymers recognise, the term "degree of substitution" (or DS) refers to substitution of the functional groups on the repeating sugar unit. In the case of cellulosic polymers, DS refers to substitution of the three hydroxyl groups on the repeating anhydroglucose unit. Thus, for cellulose polymers, the maximum degree of substitution is 3. DS values do not generally relate to the uniformity of substitution of chemical groups along the polysaccharide molecule and are not related to the molecular weight of the polysaccharide backbone. The average degree of substitution groups is preferably from 0.1 to 3 (eg. from 0.3 to 3), more preferably from 0.1 to 1 (eg. from 0.3 to 1).

The Polysaccharide before substitution

As used herein, the term "polysaccharides" includes natural polysaccharides, synthetic polysaccharides, polysaccharide derivatives and modified polysaccharides. Suitable polysaccharides for use in preparing the compounds of the present invention include, but are not limited to, gums, arabinans, galactans, seeds and mixtures thereof as well as cellulose and derivatives thereof.

Suitable polysaccharides that are useful in the present invention include polysaccharides with a degree of polymerisation (DP) over 40, preferably from about 50 to about 100,000, more preferably from about 500 to about 50,000. Constituent saccharides preferably include, but are not limited to, one or more of the following saccharides: isomaltose, isomaltotriose, isomaltotetraose, isomaltooligosaccharide, fructooligosaccharide, levooligosaccharides, galactooligosaccharide, xylooligosaccharide, gentiooligosaccharides, disaccharides, glucose, fructose, galactose, xylose, mannose, sorbose, arabinose, rhamnose, fucose, maltose, sucrose, lactose, maltulose, ribose, lyxose, allose, altrose, gulose, idose, talose, trehalose, nigerose, kojibiose, lactulose, oligosaccharides, maltooligosaccharides, trisaccharides, tetrasaccharides, pentasaccharides, hexasaccharides, oligosaccharides from partial hydrolysates of natural polysaccharide sources and mixtures thereof.

The polysaccharides can be extracted from plants, produced by organisms, such as bacteria, fungi, prokaryotes, eukaryotes, extracted from animal and/or humans. For example, xanthan gum can be produced by *Xanthomonas campestris*, gellan by *Sphingomonas paucimobilis*, xyloglucan can be extracted from tamarind seed.

The polysaccharides can be linear, or branched in a variety of ways, such as 1-2, 1-3, 1-4, 1-6, 2-3 and mixtures thereof. Many naturally occurring polysaccharides have at least some degree of branching, or at any rate, at least some saccharide rings are in the form of pendant side groups on a main polysaccharide backbone.

It is desirable that the polysaccharides of the present invention have a molecular weight in the range of from about 10,000 to about 10,000,000, more preferably from about 50,000 to about 1,000,000, most preferably from about 50,000 to about 500,000.

Preferably, the polysaccharide is selected from the group consisting of: tamarind gum (preferably consisting of xyloglucan polymers), guar gum, locust bean gum (preferably consisting of galactomannan polymers), and other industrial gums and polymers, which include, but are not limited to, Tara, Fenugreek, Aloe, Chia, Flaxseed, Psyllium seed, quince seed, xanthan, gellan, welan, rhamsan, dextran, curdlan, pullulan, scleroglucan, schizophyllan, chitin, hydroxyalkyl cellulose, arabinan (preferably from sugar beets), de-branched arabinan (preferably from sugar beets), arabinoxylan (preferably from rye and wheat flour), galactan (preferably from lupin and potatoes), pectic galactan (preferably from potatoes), galactomannan (preferably from carob, and including both low and high viscosities), glucomannan, lichenan (preferably from icelandic moss), mannan (preferably from ivory nuts), pachyman, rhamnogalacturonan, acacia gum, agar, alginates, carrageenan, chitosan, clavan, hyaluronic acid, heparin, inulin, cellodextrins, cellulose, cellulose derivatives and mixtures thereof. These polysaccharides can also be treated (preferably enzymatically) so that the best fractions of the polysaccharides are isolated.

Polysaccharides can be used which have an α- or β-linked backbone. However, more preferred polysaccharides have a β-linked backbone, preferably a β-1,4 linked backbone. It is

preferred that the β-1,4-linked polysaccharide is cellulose; a cellulose derivative, particularly cellulose sulphate, cellulose acetate, sulphoethyl cellulose, cyanoethyl cellulose, methyl cellulose, ethyl cellulose, carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylcellulose; a xyloglucan, particularly one derived from Tamarind seed gum; a glucomannan, particularly Konjac glucomannan; a galactomannan, particularly Locust Bean gum and Guar gum; a side chain branched galactomannan, particularly Xanthan gum; chitosan or a chitosan salt. Other β-1,4-linked polysaccharides having an affinity for cellulose, such as mannan, are also preferred.

The natural polysaccharides can be modified with amines (primary , secondary, tertiary), amides, esters, ethers, urethanes, alcohols, carboxylic acids, tosylates, sulfonates, sulfates, nitrates, phosphates and mixtures thereof. Such a modification can take place in position 2, 3 and/or 6 of the saccharide unit. Such modified or derivatised polysaccharides can be included in the compositions of the present invention in addition to the natural polysaccharides.

Nonlimiting examples of such modified polysaccharides include: carboxyl and hydroxymethyl substitutions (e.g. glucuronic acid instead of glucose); amino polysaccharides (amine substitution, e.g. glucosamine instead of glucose); C_1-C_6 alkylated polysaccharides; acetylated polysaccharide ethers; polysaccharides having amino acid residues attached (small fragments of glycoprotein); polysaccharides containing silicone moieties. Suitable examples of such

modified polysaccharides are commercially available from Carbomer and include, but are not limited to, amino alginates, such as hexanediamine alginate, amine functionalised cellulose-like O-methyl-(N-1,12-dodecanediamine) cellulose, biotin heparin, carboxymethylated dextran, guar polycarboxylic acid, carboxymethylated locust bean gum, carboxymethylated xanthan, chitosan phosphate, chitosan phosphate sulfate, diethylaminoethyl dextran, dodecylamide alginate, sialic acid, glucuronic acid, galacturonic acid, mannuronic acid, guluronic acid, N-acetylgluosamine, N-acetylgalactosamine, and mixtures thereof.

Especially preferred polysaccharides include cellulose, ether, ester and urethane derivatives of cellulose, particularly cellulose monoacetate, xyloglucans and galactomannans, particularly Locust Bean gum.

It is preferred that the polysaccharide has a total number of sugar units from 10 to 7000, although this figure will be dependent on the type of polysaccharide chosen, at least to some extent.

In the case of cellulose and water-soluble modified celluloses, the total number of sugar units is preferably from 50 to 1000, more preferably 50 to 750 and especially 200 to 300. The preferred molecular weight of such polysaccharides is from 10 000 to 150 000.

In the case of cellulose monoacetate, the total number of sugar units is from 10 to 200, preferably 100 to 150. The preferred molecular weight is from 10 000 to 20 000.

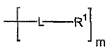
In the case of Locust Bean gum, the total number of sugar units is preferably from 50 to 7000. The preferred molecular weight is from 10 000 to 1000 000.

In the case of xyloglucan, the total number of sugar units is preferably from 1000 to 3000. the preferred molecular weight is from 250 000 to 600 000.

The polysaccharide can be linear, like in hydroxyalkyl cellulose, it can have an alternating repeat like in carrageenan, it can have an interrupted repeat like in pectin, it can be a block copolymer like in alginate, it can be branched like in dextran, or it can have a complex repeat like in xanthan. Descriptions of the polysaccharides are given in "An introduction to Polysaccharide Biotechnology", by M. Tombs and S. E. Harding, T.J. Press 1998.

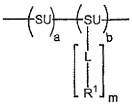
The Polymers

The polymers utilised in the invention are polysaccharides in which at least one sugar unit of the polysaccharide has been substituted by a group of the general formula



in which m, L and R^1 are as defined below.

Thus, preferred polymers have the general formula



(I)

in which each SU represents a sugar unit in a polysaccharide backbone;

a represents the number of unsubstituted sugar units as a percentage of the total number of sugar units and is in the range from 0 to 99.9%, preferably 65 to 99%, more preferably 80 to 99%;

b represents the number of substituted sugar units as a percentage of the total number of sugar units and is in the range from 0.1 to 100%, preferably 1 to 35%, more preferably 1 to 20%;

m represents the degree of substitution per sugar unit and is from 1 to 3;

L represents an ester or ether linkage; and

R^1 represents a substituted alkyl group, preferably a hydroxyalkyl, carboxyalkyl or sulfoalkyl group or a salt thereof.

Preferably, L represents a group -O-CO- or -O-.

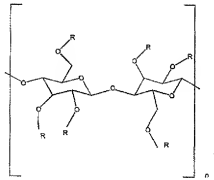
It is also preferred that R^1 is an alkyl group substituted by a group selected from -OH, $-CO-OR^2$ and $-SO_3-R^2$ where R^2

represents a hydrogen atom or an alkali metal, preferably a sodium or potassium, atom. Preferably, the alkyl group is a C_{1-6} alkyl, more preferably a C_{1-4} alkyl, group. More preferably, R_1 represents a hydroxy C_{1-4} alkyl, preferably a hydroxymethyl group, a carboxy C_{1-6} alkyl, preferably a carboxy C_{1-4} alkyl, group or a sulfo C_{2-4} alkyl, preferably a sulfoethyl, group or a sodium salt thereof. In particularly preferred embodiments, $-L-R^1$ represents a group selected from $-O-CH_2OH$, $-O-CH_2CH_2SO_3H$, $-O-CH_2-CO_2H$ and $-O-CO-CH_2CH_2CO_2H$ and sodium salts thereof.

It is preferred that the polysaccharide backbone in the polymers is β-linked, preferably β-1,4-linked.

Preferably, the polysaccharide backbone is selected from the group consisting of cellulose, cellulose derivatives (preferably cellulose sulphate, cellulose acetate, sulphoethyl cellulose, cyanoethyl cellulose, methyl cellulose, ethyl cellulose, carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylcellulose), xyloglucans (preferably those derived from Tamarind seed gum), glucomannans (preferably Konjac glucomannan), galactomannans (preferably Locust Bean gum, Guar gum and Xanthan gum), chitosan and chitosan salts. It is especially preferred that the polysaccharide backbone is Locust Bean gum or xyloglucan.

In one preferred embodiment, the polymers have the general formula:

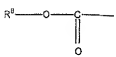


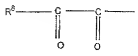
(II)

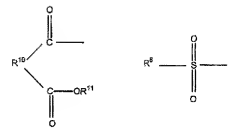
wherein at least one or more -OR groups of the polymer are independently replaced by a group

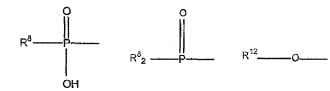
$$-L-R^1$$

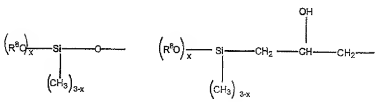
in which L and R^1 are as defined above and at least one or more R groups are independently selected from groups of formulae:-











wherein each R^8 is independently selected from C_{1-20} (preferably C_{1-6}) alkyl, C_{2-20} (preferably C_{2-6}) alkenyl (e.g. vinyl) and C_{5-7} aryl (e.g. phenyl) any of which is optionally substituted by one or more substituents independently selected from C_{1-4} alkyl, C_{1-12} (preferably C_{1-4}) alkoxy, hydroxyl, vinyl and phenyl groups;
each R^9 is independently selected from hydrogen and groups R^8 as hereinbefore defined;

R^{10} is a bond or is selected from C_{1-4} alkylene, C_{2-4} alkenylene and C_{5-7} arylene (e.g. phenylene) groups, the carbon atoms in any of these being optionally substituted by

one or more substituents independently selected from C_{1-12} (preferably C_{1-4}) alkoxy, vinyl, hydroxyl, halo and amine groups;

each R^{11} is independently selected from hydrogen, counter cations such as alkali metal (preferably Na) or $\frac{1}{2}Ca$ or $\frac{1}{2}Mg$, and groups R^8 as hereinbefore defined;

R^{12} is selected from C_{1-20} (preferably C_{1-6}) alkyl, C_{2-20} (preferably C_{2-6}) alkenyl (e.g. vinyl) and C_{5-7} aryl (e.g. phenyl), any of which is optionally substituted by one or more substituents independently selected from C_{1-4} alkyl, C_{1-12} (preferably C_{1-4}) alkoxy, hydroxyl, carboxyl, cyano, sulfonato, vinyl and phenyl groups;

x is from 1 to 3; and

groups R which together with the oxygen atom forming the linkage to the respective saccharide ring forms an ester or hemi-ester group of a tricarboxylic- or higher polycarboxylic- or other complex acid such as citric acid, an amino acid, a synthetic amino acid analogue or a protein;

any remaining R groups being selected from hydrogen and ether substituents.

It is particularly preferred that R^{12} is a methyl, ethyl, phenyl, hydroxyethyl, hydroxypropyl, carboxymethyl, sulphoethyl or cyanoethyl group.

For the avoidance of doubt, as already mentioned, in formula (II), some of the R groups may optionally have one or more

structures, for example as hereinbefore described. For example, one or more R groups may simply be hydrogen or an alkyl group.

Preferred groups may for example be independently selected from one or more of acetate, propanoate, trifluoroacetate, 2-(2-hydroxy-1-oxopropoxy) propanoate, lactate, glycolate, pyruvate, crotonate, isovalerate cinnamate, formate, salicylate, carbamate, methylcarbamate, benzoate, gluconate, methanesulphonate, toluene, sulphonate, groups and hemiester groups of fumaric, malonic, itaconic, oxalic, maleic, succinic, tartaric, aspartic, glutamic, and malic acids.

Particularly preferred such groups are the monoacetate, hemisuccinate, and 2-(2-hydroxy-1-oxopropoxy)propanoate. The term "monoacetate" is used herein to denote those acetates with the degree of substitution of about 1 or less on a cellulose or other ß-1,4 polysaccharide backbone. Thus, "cellulose monoacetate" refers to a molecule that has acetate esters in a degree of substitution of about 1.1 or less, preferably about 1.1 to about 0.5. "Cellulose triacetate" refers to a molecule that has acetate esters in a degree of substitution of about 2.7 to 3.

Cellulose esters of hydroxyacids can be obtained using the acid anhydride in acetic acid solution at 20-30°C and in any case below 50°C. When the product has dissolved the liquid is poured into water. Tri-esters can be converted to secondary products as with the triacetate. Glycollic and lactic ester are most common.

Cellulose glycollate may also be obtained from cellulose chloracetate (GB-A-320 842) by treating 100 parts with 32 parts of NaOH in alcohol added in small portions.

An alternative method of preparing cellulose esters consists in the partial displacement of the acid radical in a cellulose ester by treatment with another acid of higher ionisation constant (FR-A-702 116). The ester is heated at about 100°C with the acid which, preferably, should be a solvent for the ester. By this means cellulose acetate-oxalate, tartrate, maleate, pyruvate, salicylate and phenylglycollate have been obtained, and from cellulose tribenzoate a cellulose benzoate-pyruvate. A cellulose acetate-lactate or acetate-glycollate could be made in this way also. As an example cellulose acetate (10 g.) in dioxan (75 ml.) containing oxalic acid (10 g.) is heated at 100°C for 2 hours under reflux.

Multiple esters are prepared by variations of this process. A simple ester of cellulose, e.g. the acetate, is dissolved in a mixture of two (or three) organic acids, each of which has an ionisation constant greater than that of acetic acid (1.82×10^{-5}). With solid acids suitable solvents such as propionic acid, dioxan and ethylene dichloride are used. If a mixed cellulose ester is treated with an acid this should have an ionisation constant greater than that of either of the acids already in combination.

A cellulose acetate-lactate-pyruvate is prepared from cellulose acetate, 40 per cent. acetyl (100 g.), in a bath of 125 ml. pyruvic acid and 125 ml. of 85 per cent. lactic

acid by heating at 100°C for 18 hours. The product is soluble in water and is precipitated and washed with ether-acetone. M.p. 230-250°C.

It is preferred that m is from 1 to 2, preferably 1.

Synthesis of the Polymers

The polymers used in the present invention may be synthesised by a variety of routes which are well known to those skilled in the art of polymer chemistry. For instance, carboxyalkyl ether-linked polymers can be made by reacting a polysaccharide with a suitable haloalkanoic acid, carboxyalkyl ester-linked polymers can be made by reacting a polysaccharide with a suitable anhydride, such as succinic anhydride, and sulfoalkyl ether-linked polymers can be made by reacting a polysaccharide with a suitable alkenyl sulphonic acid.

Compositions

The substituted polysaccharide according to the first aspect of the present invention may be incorporated into compositions containing only a diluent (which may comprise solid and/or liquid) and/or also comprising an active ingredient. The compound is typically included in said compositions at levels of from 0.01% to 25% by weight, preferably from 0.05% to 15%, more preferably from 0.1% to 10%, especially from 0.1% to 5% and most preferably from 0.5% to 3%.

The active ingredient in the compositions is preferably a surface active agent or a fabric conditioning agent. More than one active ingredient may be included. For some applications a mixture of active ingredients may be used.

The compositions of the invention may be in any physical form e.g. a solid such as a powder or granules, a tablet, a solid bar, a paste, gel or liquid, especially, an aqueous based liquid. In particular the compositions may be used in laundry compositions, especially in liquid, powder or tablet laundry composition.

The compositions of the present invention are preferably laundry compositions, especially main wash (fabric washing) compositions or rinse-added softening compositions. The main wash compositions may include a fabric softening agent and rinse-added fabric softening compositions may include

surface-active compounds, particularly non-ionic surface-active compounds, if appropriate.

The detergent compositions of the invention may contain a surface-active compound (surfactant) which may be chosen from soap and non-soap anionic, cationic, non-ionic, amphoteric and zwitterionic surface-active compounds and mixtures thereof. Many suitable surface-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and non-ionic compounds.

The compositions of the invention may contain linear alkylbenzene sulphonate, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}. It is preferred if the level of linear alkylbenzene sulphonate is from 0 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

The compositions of the invention may contain other anionic surfactants in amounts additional to the percentages quoted above. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The compositions of the invention may also contain non-ionic surfactant. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

It is preferred if the level of non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

Any conventional fabric conditioning agent may be used in the compositions of the present invention. The conditioning agents may be cationic or non-ionic. If the fabric conditioning compound is to be employed in a main wash detergent composition the compound will typically be non-ionic. For use in the rinse phase, typically they will be cationic. They may for example be used in amounts from 0.5% to 35%, preferably from 1% to 30% more preferably from 3% to 25% by weight of the composition.

Preferably the fabric conditioning agent(s) have two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16}. Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long

chain alkyl or alkenyl groups of the fabric conditioning agents are predominantly linear.

The fabric conditioning agents are preferably compounds that provide excellent softening, and are characterised by a chain melting Lβ to Lα transition temperature greater than 25°C, preferably greater than 35°C, most preferably greater than 45°C. This Lβ to Lα transition can be measured by DSC as defined in " Handbook of Lipid Bilayers, D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

Substantially insoluble fabric conditioning compounds in the context of this invention are defined as fabric conditioning compounds having a solubility less than 1×10^{-3} wt % in demineraillised water at 20°C. Preferably the fabric softening compounds have a solubility less than 1×10^{-4} wt %, most preferably less than 1×10^{-8} to 1×10^{-6}. Preferred cationic fabric softening agents comprise a substantially water insoluble quaternary ammonium material comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20} or, more preferably, a compound comprising a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C_{14}.

Preferably, the cationic fabric softening agent is a quaternary ammonium material or a quaternary ammonium material containing at least one ester group. The quaternary ammonium compounds containing at least one ester group are referred to herein as ester-linked quaternary ammonium compounds.

As used in the context of the quarternary ammonium cationic fabric softening agents, the term 'ester group', includes an ester group which is a linking group in the molecule.

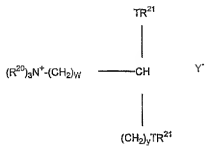
It is preferred for the ester-linked quaternary ammonium compounds to contain two or more ester groups. In both monoester and the diester quaternary ammonium compounds it is preferred if the ester group(s) is a linking group between the nitrogen atom and an alkyl group. The ester groups(s) are preferably attached to the nitrogen atom via another hydrocarbyl group.

Also preferred are quaternary ammonium compounds containing at least one ester group, preferably two, wherein at least one higher molecular weight group containing at least one ester group and two or three lower molecular weight groups are linked to a common nitrogen atom to produce a cation and wherein the electrically balancing anion is a halide, acetate or lower alkosulphate ion, such as chloride or methosulphate. The higher molecular weight substituent on the nitrogen is preferably a higher alkyl group, containing 12 to 28, preferably 12 to 22, e.g. 12 to 20 carbon atoms, such as coco-alkyl, tallowalkyl, hydrogenated tallowalkyl or substituted higher alkyl, and the lower molecular weight substituents are preferably lower alkyl of 1 to 4 carbon atoms, such as methyl or ethyl, or substituted lower alkyl. One or more of the said lower molecular weight substituents may include an aryl moiety or may be replaced by an aryl, such as benzyl, phenyl or other suitable substituents.

Preferably the quaternary ammonium material is a compound having two C_{12}-C_{22} alkyl or alkenyl groups connected to a quaternary ammonium head group via at least one ester link, preferably two ester links or a compound comprising a single long chain with an average chain length equal to or greater than C_{20}.

More preferably, the quaternary ammonium material comprises a compound having two long chain alkyl or alkenyl chains with an average chain length equal to or greater than C_{14}. Even more preferably each chain has an average chain length equal to or greater than C_{16}. Most preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C_{16}. It is preferred if the long chain alkyl or alkenyl groups are predominantly linear.

The most preferred type of ester-linked quaternary ammonium material that can be used in laundry rinse compositions according to the invention is represented by the formula (A):



wherein T is $-O-\overset{O}{\overset{\|}{C}}-$ or $-\overset{O}{\overset{\|}{C}}-O-$; each R^{20} group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^{21} group is independently selected from C_{8-28} alkyl or alkenyl groups; Y^- is any suitable counter-ion, i.e. a halide, acetate or lower alkosulphate ion, such as chloride or methosulphate;

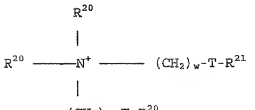
w is an integer from 1-5 or is 0; and
y is an integer from 1-5.

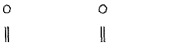
It is especially preferred that each R^{20} group is methyl and w is 1 or 2.

It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

Preferred materials of this class such as 1,2 bis[hardened tallowoyloxyl-3-trimethylammonium propane chloride and their method of preparation are, for example, described in US-A-4 137 180. Preferably these materials comprise small amounts of the corresponding monoester as described in US-A-4 137 180 for example 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

Another class of preferred ester-linked quaternary ammonium materials for use in laundry rinse compositions according to the invention can be represented by the formula:

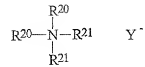
(B) 

wherein T is  and

wherein R^{20}, R^{21}, w, and Y^- are as defined above.

Of the compounds of formula (B), di-(tallowyloxyethyl)-dimethyl ammonium chloride, available from Hoechst, is the most preferred. Di-(hardened tallowyloxyethyl)dimethyl ammonium chloride, ex Hoechst and di-(tallowyloxyethyl)-methyl hydroxyethyl methosulphate are also preferred.

Another preferred class of quaternary ammonium cationic fabric softening agent is defined by formula (C):-

(C) 

where R^{20}, R^{21} and Y^- are as hereinbefore defined.

A preferred material of formula (C) is di-hardened tallow-diethyl ammonium chloride, sold under the Trademark Arquad 2HT.

The optionally ester-linked quaternary ammonium material may contain optional additional components, as known in the art, in particular, low molecular weight solvents, for instance isopropanol and/or ethanol, and co-actives such as nonionic softeners, for example fatty acid or sorbitan esters.

The compositions of the invention, when used as main wash fabric washing compositions, will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will typically range from 5 to 80 wt%, preferably from 10 to 60 wt%.

It is also possible to include certain mono-alkyl cationic surfactants which can be used in main-wash compositions for fabrics. Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

The choice of surface-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions,

different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate. Typically the compositions will comprise at least 2 wt% surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap.

The compositions of the invention, when used as main wash fabric washing compositions, will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will typically range from 5 to 80 wt%, preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as

disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: $0.8\text{-}1.5\ Na_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite

he compositions of the invention is
P (zeolite MAP) as described and
nilever). Zeolite MAP is defined as
icate of the zeolite P type having
io not exceeding 1.33, preferably
.90 to 1.33, and more preferably
90 to 1.20.

ite MAP having a silicon to
g 1.07, more preferably about
pacity of zeolite MAP is
per g of anhydrous material.

resent include polycarboxylates
, acrylic/maleic copolymers,
meric polycarboxylates such as
inates, glycerol mono-, di
loxy succinates,
olinates,
yl- and alkenylmalonates and
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pecially acrylic/maleic
s of from 0.5 to 15 wt%,

, are preferably present
um salt, form.

builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethyloxy succinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pernoanoic acid precursors. Especially preferred bleach

precursors suitable for use in the present invention are N,N,N',N',-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever), and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) are also of interest.

The bleach system can be either supplemented with or replaced by a peroxyacid. examples of such peracids can be found in US 4 686 063 and US 5 397 501 (Unilever). A preferred example is the imido peroxycarboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phthalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

A bleach stabiliser (transition metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.

An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A ,EP 458 398A and EP 509 787A (Unilever).

The compositions according to the invention may also contain one or more enzyme(s).

Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilins which are obtained from particular strains of B. Subtilis B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles

Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).

Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used.

The compositions of the invention may contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate copolymer, or sodium silicate. One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; soil release polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; foam controllers and decoupling polymers. Further additional ingredients include surfactants, detergency builders, bleaches, transition metal sequestrants, enzymes, fabric softening and/or conditioning agents, lubricants for inhibition of

fibre damage and/or for colour care and/or for crease reduction and/or for ease of ironing, UV absorbers such as fluorescers and photofading inhibitors, for example sunscreens/UV inhibitors and/or anti-oxidants, fungicides, insect repellents and/or insecticides, perfumes, dye fixatives, waterproofing agents, deposition aids, flocculants, anti-redeposition agents and soil release agents. These lists are not intended to be exhaustive. However, many of these ingredients will be better delivered as benefit agent groups in materials according to the first aspect of the invention.

The detergent composition when diluted in the wash liquor (during a typical wash cycle) will typically give a pH of the wash liquor from 7 to 10.5 for a main wash detergent.

Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or post-dosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/llitre, more preferably at least 500 g/litre. Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

Substrate

The substrate may be any substrate onto which it is desirable to deposit a polymer and which is subjected to treatment such as a washing or rinsing process.

In particular, the substrate may be a textile fabric, fabric, preferably of cotton.

It has been found that particular good results are achieved when using a natural fabric substrate such as cotton, or fabric blends containing cotton.

Treatment

The treatment of the substrate with the material of the invention can be made by any suitable method such as washing, soaking or rinsing of the substrate.

Typically the treatment will involve a washing or rinsing method such as treatment in the main wash or rinse cycle of a washing machine and involves contacting the substrate with an aqueous medium comprising the material of the invention.

The present invention will now be explained in more detail by reference to the following non-limiting examples:-

Example 1

Preparation of carboxymethylated Locust Bean Gum (L = -O-; R^1 = $-CH_2CO_2Na$)

Locust Bean Gum (MUD 246B, ex Rhodia) (5g, 30.84 mmol of anhydrosugar units) was dispersed in a mixture of demineralised water (12 ml) and propan-2-ol (30 ml) with vigorous stirring in a 2-necked 100ml round bottom flask fitted with a mechanical stirrer. After heating the solution to 70°C, sodium hydroxide (0.625g, 15.6 mmol) was added and the mixture stirred for 15 minutes at the reaction temperature. Sodium chloroacetate (1.8g, 15 mmol) was then added as a solution in demineralised water (2 ml) and the reaction mixture vigorously stirred for 15 minutes at 70°C. The same protocol of adding both reagents was repeated three times and the reaction mixture stirred for 6 hours whilst maintaining the temperature at 70°C. The reaction mixture was then poured into methanol (200ml) and the resultant white precipitate collected on a sinter funnel. The product was

washed repeatedly with methanol to remove glycolic acid. The product was then re-dispersed into hot demineralised water, resulting in a highly viscous solution. This was freeze dried resulting in 4.75g of white material.

IR: 1598cm^{-1} (s, carboxylate ion)

^{1}H-NMR (500MHz):

Prior to analysis the sample was de-polymerised by acid hydrolysis using a solution of 20% DCl in D_2O heated for 1 hour at 80°C:

4-4.8 ppm (6H, sugar H); 4.94 ppm (0.32H, glycolate CH_2); 5.25-5.95 ppm (1H, anomeric H). This corresponds to a degree of substitution by glycolate ester groups of 0.15.

Example 2

Preparation of sulfoethylated Locust Bean Gum (L= -O-; R^1 = -$CH_2CH_2SO_3Na$)

Locust Bean Gum (MUD 246B, ex Rhodia) (5g, 30.84 mmol of anhydrosugar units) was dispersed in a mixture of demineralised water (12 ml) and propan-2-ol (30 ml) with vigorous stirring in a 2-necked 100ml round bottom flask fitted with a mechanical stirrer. After heating the solution to 70°C, sodium hydroxide (0.625g, 15.6 mmol) was added as a solution in water (2 ml) and the mixture stirred for 15 minutes at the reaction temperature. Vinyl sulfonic acid (8 ml of a 25% aqueous solution, 15.6 mmol) was added and the

reaction mixture vigorously stirred for 15 minutes at 70°C. The same protocol of adding both reagents was repeated three times and the reaction mixture stirred for 6 hours whilst maintaining the temperature at 70°C. The reaction mixture was then poured into methanol (200ml) and the resultant white precipitate collected on a sinter funnel. The product was washed repeatedly with methanol and then re-dispersed into hot demineralised water. This was freeze dried resulting in 6.25g of creamy coloured material.

IR: $1079cm^{-1}$, $1155cm^{-1}$ (s, sulfonic acid salts).

Example 3

Prepartion of succinoylated Locust Bean Gum (L= -O-CO-; R^1 $=CH_2CH_2CO_2H$)

A 9% w/v solution of lithium chloride in anhydrous dimethylsulfoxide (DMSO) was prepared by heating 100 ml of the solvent to 150°C in a 2-necked round bottom flask fitted with a mechanical stirrer. Locust Bean Gum (MUD 246B, ex Rhodia) (5g, 30.84 mmol of anhydrosugar units) was added whilst maintaining the temperature until a highly viscous, homogeneous solution had formed. After cooling the solution to 40°C, succinic anhydride (4.5g, 45 mmol) was added as a solution in anhydrous dimethyl sulphoxide (DMSO) (10ml) followed by the addition of 4-(dimethylamino)pyridine (1.15g, 9.4 mmol), also as a solution in DMSO (10ml). The mixture was stirred at 40°C for 16 hours. The reaction mixture was then poured into methanol (300ml) and the resultant white precipitate collected on a sinter funnel After repeated

washing with methanol the product was dried, then re-dispersed into hot demineralised water. This was freeze dried resulting in 4.54g of creamy coloured material.

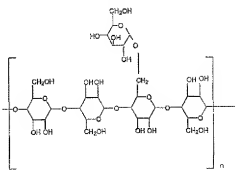
IR: $1720cm^{-1}$ (vs, aliphatic ester carbonyl)

Example 4

Determination of degree of substitution (DS) using base hydrolysis:

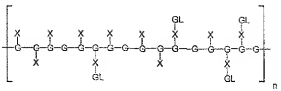
Locust Bean Gum-succinate, as prepared above (1.355g) was added to a conical flask, to which 25ml of 1M sodium hydroxide solution was added. This was repeated with a sample of the unmodified Locust Bean Gum (0.5g) as a blank. The flasks were stoppered and left at ambient temperature overnight. Each flask was then titrated with 1M hydrochloric acid solution using phenolphthalein as indicator. The amount of acid required for neutralisation allows the number of the succinic acid molecules present to be calculated. For this example, the Locust Bean Gum derivative was found to be 53% succinoylated.

Structure of a repeat unit of Locust Bean Gum:



Locust bean gum
copolymer with a backbone of (1,4)-linked ß-D-mannose units having side stubs of (1,6)-linked α-D-galactose groups in a ratio of mannose to galactose = 4 :1

Structure of a repeat unit of Tamarind Seed Xyloglucan



Xyloglucan
copolymer with a β-D-glucose-(1,4)-β-D-glucose backbone containing β-D-galactose-(1,2)-α-D-xylose-(1,6)-β-D-glucose side chains

Example 5

Soil Release Evaluation on Cotton Using Dirty Motor Oil Stain

Padding

Per tray
- 400 -500 cm^3 of copolymer solution (sufficient to cover cloth)
- 1 piece of cotton, 12" x 9", of known weight, marked into 12 3" x 3" squares
- soak for 30 mins.
- hand wring to remove excess polymer solution and reweigh (wet).
- fabric dried overnight on a flat surface at ambient temperature and then cut into 3" x 3" squares.

Staining (Dirty Motor Oil)

- pipette 0.15 cm^3 of a 15% dirty motor oil (DMO) in toluene solution into the centre of each piece of fabric in a fume cupboard.
- allow to wick at ambient temperature overnight (cloths should be left in the fume cupboard for at least 2 hrs).

Washing

Per pot
- 1 litre of wash liquor [(1)] or demineralised water.
- reference pots 8 untreated cloths.
- sample pots 8 polymer treated cloths.
- wash at 30°C for 15 mins, tergotometer speed 72rpm.
- rinse, 1 litre demineralised water, 5 mins.

- fabric dried overnight on a flat surface at ambient temperature.

Reflectance

- reflectance of cloths is measured before staining/after padding, after staining/before washing and after washing.
- place 3 pieces of clean cotton cloth behind the sample being measured.
- take 1 reading per piece of fabric.

(1) - 10cm^3 LAS stock solution (12.3 g 48% LAS paste in 100 cm^3 demineralised water).
- 5 cm^3 $CaCl_2.2H_2O$ stock solution (0.41g $CaCl_2,2H_2O$ in 100 cm^3 demineralised water).
- 20 cm^3 Solution A (30 g NaCl, 33g Na TPP and 37.5 g Na_2CO_3 in 1000 cm^3 demineralised water).
- make up to 1 litre with demineralised water.

LAS = linear alkylbenzene sulphonate
NaTPP = Sodium tripolyphosphate
Detergency used 0.5% w/w polymer

Results:

Sample	Δ R (Washed / Soiled)	
	no surfactant +/-	surfactant +/-
CONTROL 1	5.3	10.4
	0.9	0.8
CM-XG	8.1	13.0
4:1	0.4	0.4
CM-XG	8.0	13.0
3:1	0.6	0.6
CM-XG	8.5	14.4
2:1	0.4	0.2
CM-XG	8.5	12.9
1:1	0.4	0.3
CM-XG	8.3	13.5
0.5:1	0.6	0.5
CM-LBG	8.1	13.0
4:1	0.3	0.5
CM-LBG	8.4	13.2
3:1	0.3	0.4
CM-LBG	8.1	13.8
2:1	0.4	0.3
CM-LBG	9.4	12.7
1:1	0.5	0.5
CM-LBG	6.8	11.6
0.5:1	0.6	0.3
SU-XG	6.6	11.9
53	0.5	0.6
SU-XG	7.3	12.2
33	0.5	0.4
SU-XG	8.4	11.3
26	0.3	0.3
SU-XG	7.5	10.8
14	0.7	0.7
SU-XG	7.3	11.8
10	0.4	0.4
SU-LBG	8.0	10.6
10	0.4	0.2
SU-LBG	7.6	11.1
8	0.4	0.6
SU-LBG	8.1	12.4
5.5	0.4	0.3
SU-LBG	7.5	10.9
3.8	0.3	0.7
SU-LBG	7.9	12.4
1.9	0.2	0.6

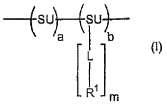
Xyloglucan	7.1	11.0
Locust Bean Gum	0.4	0.6
	5.2	10.1
	0.5	0.4

	Δ R (washed /Soiled)	
Sample	no Surfactant +/-	surfactant +/-
Su-Et XG 4:1	7.6 0.7	12.5 0.17
Su-Et XG 3:1	7.6 0.5	12.4 0.5
Su-Et XG 2:1	7.2 0.4	11.8 0.6
Su-Et XG 1:1	6.7 0.6	12.3 0.4
Su-Et XG 0.5:1	6.5 0.4	10.9 0.7
Su-Et LBG 4:1	7.3 0.3	11.4 0.4
Su-Et LBG 3:1	7.4 0.4	11.8 0.5
Su-Et LBG 2:1	7.6 0.5	12.4 0.7
Su-Et LBG 1:1	7.3 0.5	11.8 0.5
Su-Et LBG 0.5:1	7.3 0.8	12.3 0.3
Control	4.8 0.3	9.5 0.5

CM-XG = carboxymethylated xyloglucan
CM-LBG = carboxymethylated Locust Bean Gum
SU-XG = succinoylated xyloglucan
SU-LBG = succinoylated Locust Bean Gum
Su-Et XG = sulfoethylated xyloglucan
Su-Et XG = sulfoethylated Locust Bean Gum

CLAIMS

1. Use of a polymer for promoting soil release during laundering of a textile fabric, characterised in that the polymer has the general formula I:-



(I)

in which each SU represents a sugar unit in a polysaccharide backbone;

a represents the number of unsubstituted sugar units as a percentage of the total number of sugar units and is in the range from 0 to 99.9%, preferably 65 to 99%, more preferably 80 to 99%;

b represents the number of substituted sugar units as a percentage of the total number of sugar units and is in the range from 0.1 to 100%, preferably 1 to 35%, more preferably 1 to 20%;

m represents the degree of substitution per sugar unit and is from 1 to 3;

L represents an ester or ether linkage; and

R^1 represents a substituted alkyl group, preferably a hydroxyalkyl, carboxyalkyl or sulfoalkyl group or a salt thereof.

2. Use according to claim 1 characterised in that L represents a group -O-CO- or -O-.

3. Use according to claim 1 or claim 2 characterised in that R^1 is an alkyl group substituted by a group selected from -OH, -CO-OR^2 and -SO_3-R^2 where R^2 represents a hydrogen atom or an alkali metal, preferably a sodium or potassium, atom.

4. Use according to any one of the preceding claims characterised in that the alkyl group is a C_{1-6} alkyl, preferably a C_{1-4} alkyl, group.

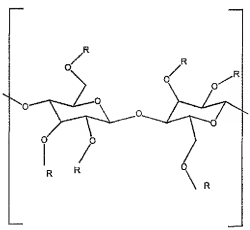
5. Use according to any one of the preceding claims characterised in that R^1 represents a hydroxy C_{1-4} alkyl, preferably a hydroxymethyl, group, a carboxy C_{1-5} alkyl, preferably a carboxy C_{1-4} alkyl, group or a sulfo C_{2-4} alkyl, preferably a sulfoethyl, group or a sodium salt thereof.

6. Use according to any one of the preceding claims characterised in that $-L-R^1$ represents a group selected from $-O-CH_2OH$, $-O-CH_2CH_2SO_3H$, $-O-CH_2-CO_2H$ and $-O-CO-CH_2CH_2CO_2H$ and sodium salts thereof.

7. Use according to any one of the preceding claims characterised in that the polysaccharide backbone is β-1,4-linked.

8. Use according to any one of the preceding claims characterised in that the polysaccharide backbone is selected from the group consisting of cellulose, cellulose derivatives, xyloglucans, glucomannans, galactomannans, chitosan and chitosan salts.

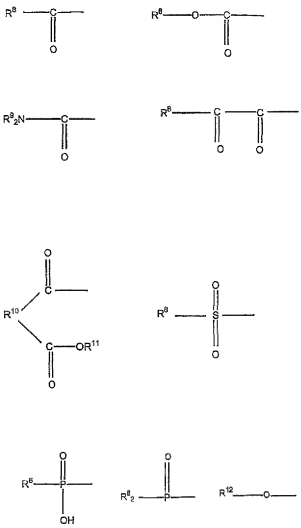
9. Use according to any one of the preceding claims, characterised in that the polymer has the general formula

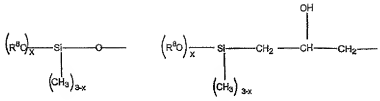


(II)

in which at least one or more -OR groups of the polymer are independently replaced by a group -L-R^1

in which L and R^1 are as defined in any one of the preceding claims, and at least one or more R groups are independently selected from hydrogen atoms and groups of formulae:-





in which each R^8 is independently selected from C_{1-20} alkyl, C_{2-20} alkenyl and C_{5-7} aryl any of which is optionally substituted by one or more substituents independently selected from C_{1-4} alkyl, C_{1-12} alkoxy, hydroxyl, vinyl and phenyl groups;

each R^9 is independently selected from hydrogen and groups R^8 as hereinbefore defined;

R^{10} is a bond or is selected from C_{1-4} alkylene, C_{2-4} alkenylene and C_{5-7} arylene groups, the carbon atoms in any of these being optionally substituted by one or more substituents independently selected from C_{1-12} alkoxy, vinyl, hydroxyl, halo and amine groups;

each R^{11} is independently selected from hydrogen, counter cations and groups R^8 as hereinbefore defined;

R^{12} is selected from C_{1-20} alkyl, C_{2-20} alkenyl and C_{5-7} aryl, any of which is optionally substituted by one or more substituents independently selected from C_{1-4} alkyl, C_{1-12} alkoxy, hydroxyl, carboxyl, cyano, sulfonato, vinyl and phenyl groups;

x is from 1 to 3; and

groups R which together with the oxygen atom forming the linkage to the respective saccharide ring forms an ester or hemi-ester group of a tricarboxylic- or higher polycarboxylic acid, an amino acid, a synthetic amino acid analogue or a protein;

any remaining R groups being selected from hydrogen and ether substituents.

10. Use according to any one of the preceding claims characterised in that m is from 1 to 2.

11. Use according to any one of the preceding claims, characterised in that the polysaccharide backbone has a number average molecular weight from 10000 to 1000000.

12. A method of promoting soil release during laundering of a textile fabric, characterised in that the method comprises contacting the fabric with a polymer as defined in any one of the preceding claims and subsequently washing the fabric after wear or use of the fabric.

13. Use of a polymer in the manufacture of a laundry cleaning composition for effecting soil release from a laundry item, characterised in that the compound is a polymer as defined in any one of the preceding claims.

14. Use according to claim 13 characterised in that the laundry cleaning composition comprises from 0.01% to 25% of the polymer by weight of the total composition.

INTERNATIONAL SEARCH REPORT

Intl Application No
PCT/EP 02/10586

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 65015 A (PROCTER & GAMBLE) 2 November 2000 (2000-11-02) page 18 -page 20; claims ---	1-14
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search	Date of mailing of the international search report
11 December 2002	19/12/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax (+31–70) 340–3016	Serbetsoglou, A

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A	WO 00 18861 A (UNILEVER) 6 April 2000 (2000-04-06) cited in the application claims	1-9
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Int. ional Application No
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